

Periodic orbits localization through energy frequency analysis in bound systems

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Density of states (DOS) plays a central role in statistical physics. The knowledge of DOS is essential to characterize semiconductors, bio-systems, rate processes and to calculate partition functions. The calculation of the exact DOS is complicated because in the general case the energy levels of molecular systems are unknown. In practice we need to separate the different degrees of freedom and treat the system in the rigid rotor and harmonic picture to evaluate the DOS. In absence of anharmonicities and ro-vibrational couplings this static treatment of the problem results a poor description of the DOS. A dynamical treatment of the problem would be needed to include all of this missing factors. Molecular dynamics is an elegant way to calculate the vibrational spectrum of molecules to include the all of the anharmonicities, the couplings between vibrational and rotational modes and the contribution from large amplitude (torsional) motions.

In our work we have developed a molecular dynamics based approach where the kinetic energy spectrum is used to localize the periodic orbits. An extended normal mode like ansatz is introduced to decompose the phase space into harmonic periodic orbits. The kinetic energy spectrum is fitted by this ansatz to extract the fundamental frequencies of the system. Such kind of representation of the dynamics allows to preserve the simple normal mode like picture by renormalizing the harmonic frequencies. However, now the frequencies depend on the total energy and angular momentum of the system: $\omega(E, J)$. The evaluation of the DOS is straightforward by using the renormalized harmonic frequencies. Furthermore, our approach is a natural way to characterize the coupling between the renormalized harmonic modes.

References

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